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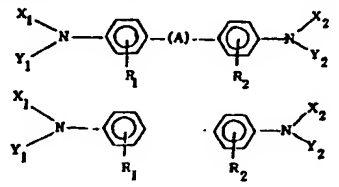
(54) Electrophotographic Photosensitive Member

(57) The invention relates to an electrophotographic photosensitive body of the kind comprising a conductive support, a photoconductive layer and a protective layer. With a view to enabling the body to be imaged by the conventional Carlson process while having stable electrical and mechanical operating characteristics even under varying temperature and humidity conditions, the protective layer contains in a binder resin an aromatic amine compound of formula (I) or (II) below and a salt having an oxidising ability:



wherein X_1, X_2, Y_1, and Y_2 each independently represents an alkyl group or a substituted aryl group, R_1 and R_2 each independently represents a hydrogen atom, an alkyl group containing 1 to 6 carbon atoms, or a halogen atom, and —(A)— represents a member selected from certain divalent aromatic and heterocyclic radicals.

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SPECIFICATION

Electrophotographic Photosensitive Member

This invention relates to an electrophotographic photosensitive body for use in an electrophotographic process known as the Carlson process, which comprises a conductive support having provided thereon in sequence a photoconductive layer and a surface-protecting layer.

Typical electrophotographic bodies which have so far been used include those comprising a conductive base having deposited thereon a photosensitive layer of Se, Se-Te alloy, Se-As alloy, or the like, and those comprising a conductive support having coated thereon an organic photoconductor like PVK (polyvinylcarbazole)-TNF (2,4,7-trinitrofluorenone). However, they have the defects that, in repeated uses, they are liable to suffer delamination or be damaged during removal of residual toner, or that the photosensitive layer is liable to be worn so easily that it must be replaced in a comparatively early stage. It is known to provide a protective surface layer on the photosensitive body to overcome these disadvantages. One such surface layer is an insulating layer comprising a material with comparatively high dielectric properties. This insulating layer has the advantage that it can be present as a thick layer and be of a comparatively high mechanical strength. However, in order to repeatedly use this type of photosensitive body, there is required a special latent image-forming process such as first charging, second charging with an opposite polarity, then imagewise exposure, or first charging, second charging with simultaneous imagewise exposure, then uniform exposure. These processes require two or more charging steps in one copying procedure, which requires complicated apparatuses leading to unstable characteristics and high cost.

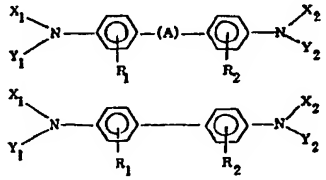
An imaging member which does not require the aforesaid special latent image-forming process and which can be used for the so-called Carlson process of charging in the dark followed by imagewise exposure is the member of the present invention having a specific protective layer. This protective layer must be made less insulating to prevent electric charge from accumulating on or in the protective layer.

In conventionally employed processes, a quaternary ammonium salt or the like is added to the protective layer. Generally, however, conductivity of such materials greatly varies due to absorption of ambient moisture. In a dry state, conductivity of the protective layer is reduced so much that charge will accumulate, resulting in fogging of images, whereas in a highly humid state, conductivity increases more than is necessary, and hence charge migration will take place in a lateral direction, resulting in blurring of images. Further, for use in the Carlson process, the conventional protective layer must be comparatively thin, i.e., not more than several microns, which is unsatisfactory from the point of view of mechanical strength. In addition, materials added for lowering insulating properties color the protective layer, which causes detrimental influences on spectral sensitivity of the light-sensitive body.

This invention relates to a photosensitive body having a protective layer usable in the aforesaid Carlson process. An object of the present invention is to provide a photosensitive body which does not suffer from the accumulation of charge in repeated uses. Another object is to provide a photosensitive body which is stable to changing ambient conditions, and which shows favorable optical properties even though comparatively thick.

The present invention is an electrophotographic photosensitive body having on the surface of a photoconductive layer a protective layer comprising a specific aromatic amine compound and a salt having an oxidizing ability dispersed in a binder resin.

The aromatic amine compounds to be used in the present invention are represented by following general formula (I) or (II):



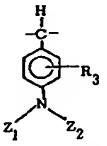
(I)

(II)

wherein X_1, X_2, Y_1, and Y_2 each independently represents an alkyl group or a substituted or unsubstituted aryl group, R_1 and R_2 each independently represents a hydrogen atom, an alkyl group containing 1—6 carbon atoms, or a halogen atom, and —(A)— represents a member selected from the group consisting of (III)—(IX) wherein

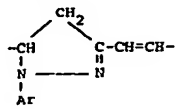
is (III)

is (IV)



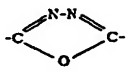
is (V)

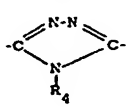
wherein Z_1 and Z_2 each independently represents an alkyl group containing 1—6 carbon atoms, or a substituted or unsubstituted aryl group, and R_3 represents a hydrogen atom or an alkyl group containing 1—6 carbon atoms,



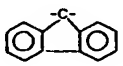
is (VI)

wherein Ar represents a substituted or unsubstituted aryl group,

 is (VII)

 is (VIII)

wherein R_4 represents an alkyl group containing 1—6 carbon atoms, and

 is (IX)

The binder resin to be used in the protective layer of the present invention can be a polyester resin, polycarbonate resin, polystyrene resin, polyurethane resin, epoxy resin, acrylic resin, polyvinyl chloride resin, vinyl chloride-vinyl acetate copolymer resin, for example.

As the salt having an oxidizing ability to be used in the present invention, there are illustrated salts of optional combinations between an anion such as $[SbCl_6]^-$, $[SbCl_4]^-$, $[PF_6]^-$, $[BF_4]^-$, $[C10_4]^-$, etc. and a cation such as [tropylium]$^+$, [triphenylmethyl]$^+$, [(p-bromophenyl)ammonium]$^+$, [tetraethylammonium]$^+$, [benzyldimethylphenylammonium]$^+$, [2,4,6-trimethylpyrylium]$^+$, Ag^+, K^+, Na^+, etc.

The composition ratio in the protective layer varies depending upon the combination of the materials, but it is preferable to add 5—100 parts by weight of the aromatic amine compound and 0.01—10 parts by weight of said salt material per 100 parts by weight of the binder resin. Selection of the composition ratio within the above-described range permits one to form a protective layer having a thickness of up to 15—20 μ or more. The thickness of the protective layer is preferably from about 2—30 μ.

The photoconductive layer of the present invention can be a deposited film of Se, Se-Te alloy, Se-As alloy, Se-Sb alloy, Se-Bi alloy, or the like. It also can be a coating of an organic photoconductor, such as PVK/TNF, or an inorganic photoconductor like ZnO or CdS dispersed in a binder, or a stratum of a charge-generating layer and a charge transfer layer. It is particularly noteworthy that photoconductors which cannot be used in ordinary electrophotographic processes due to weak mechanical strength can be used in the present invention.

In the present invention, photogeneration of charge carriers is conducted in the photoconductive layer, and hence the protective layer must be substantially transparent to transmit light to which the photoconductive layer is sensitive. Also, an interlayer may be provided in the present invention between the protective layer and the photoconductive layer to improve adhesiveness or charge-retaining property.

The photosensitive body of the present invention is fundamentally different from the conventional photosensitive body known as stratum type photosensitive body comprising a conductive base having provided thereon a charge-generating layer and a charge transfer layer. That is, in the photosensitive body in accordance with the present invention, charge pattern is formed between a protective layer photoconductive interface and a conductive base. On the other hand, in the conventional stratum type light-sensitive body, charge pattern is formed between the surface of the charge transfer layer and the conductive base. In addition, with the protective layer, the electrostatic charge must be implanted from the surface of the protective layer into the protective layerphotoconductive interface, whereas with the charge transfer layer, charge must stay on the surface. Further, the protective layer is thin in thickness as compared with the photoconductive layer so as to produce enough difference in electric potential between light portions and dark portions, whereas the charge transfer layer must be thicker than the charge-generating layer. Thus, the protective layer of the present invention is required to have different functions and different interfacial properties.

The electrophotographic photosensitive body of the present invention constituted as stated above has various advantages over conventional ones. That is:

(1) it has a surface layer which permits the formation of a latent image without employing a special process;

(2) when repeatedly used, there is substantially no accumulation and increase of residual charge;

(3) it is generally unaffected by change in ambient temperature and humidity;

(4) the thickness of the protective layer can be made comparatively thick;

(5) the structure includes a protective layer which does not substantially influence the photosensitivity of the photosensitive layer; and

(6) the structure includes a protective layer having high mechanical strength.

The present invention will be described in more detail by the following Examples.

Example 1

20 parts by weight of 1-phenyl-3-(p-dimethylaminostyryl)-5-(p-dimethylaminophenyl)pyrazoline and 1 part by weight of silver perchlorate were added to 100 parts by weight of a polyester resin (trade name: Du Pont 49000; made by E. I. du Pont de Nemours & Co., Inc.), and dissolved in tetrahydrofuran. The resulting solution was coated on an amorphous selenium deposited film (60 μ thick) provided on an aluminum base, and dried to obtain a photosensitive body having a 15-μ thick protective layer. When steps of positive charging, imagewise exposure, development, transfer, and cleaning were repeated using this photosensitive body, excellent copies were consistently obtained.

Example 2

40 parts by weight of 2,5-bis(4-diethylaminophenyl)-oxadiazole-1,3,4 and 0.5 part by weight of tropylium tetrafluoroborate were added to 100 parts by weight of a polyester resin (trade name: Viron 200; made by Toyo Spinning Co., Ltd.), and dissolved in dichloromethane. The resulting solution was coated on a As_2Se_3 deposited film (55 μ thick) provided on an aluminum base, and dried to obtain a photosensitive body having a 15-μ thick protective layer. When this photosensitive body was tested in the same manner as in Example 1, excellent copies were consistently obtained.

Example 3

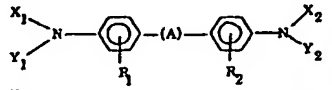
15 parts by weight of 4,4'-bis(N,N'-diethylamino)-triphenymethane and 0.1 part by weight of tropylium hexachloroantimonate were added to 100 parts by weight of a polycarbonate resin (trade name: Panlite N; made by Teijin Chemicals, Ltd.), and dissolved in dichloromethane. The resulting solution was coated on a Se-Te alloy deposited film (60 μ thick) provided on an aluminum base, followed by drying to obtain a photosensitive body having a 10-μ thick protective layer. When this photosensitive body was tested in the same manner as in Example 1, excellent copies were consistently obtained.

The present invention comprehends an electrophotographic imaging apparatus comprising: an electrophotographic photosensitive body in accordance with the invention; means to uniformly electrostatically charge said body; means to expose the photoconductive layer of the thus-charged body imagewise to actinic electromagnetic radiation to form an electrostatic latent image; and means to develop the electrostatic latent image.

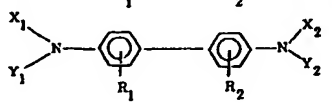
The present invention further comprehends an electrophotographic imaging method, the method comprising: uniformly elctrostatically charging an electrophotographic photosensitive body in accordance with the invention; imagewise exposing the photoconductive layer of the thus-charged body to actinic electromagnetic radiation to form an electrostatic latent image; and developing the electrostatic latent image.

Claims

1. An electrophotographic photosensitive body comprising a conductive support having provided thereon, in sequence, a photoconductive layer and a protective layer, said protective layer containing in a binder resin an aromatic amine compound represented by following general formula (I) or (II) and a salt having an oxidizing ability:



(I)

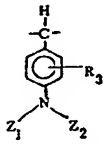


(II)

wherein X_1, X_2, Y_1, and Y_2 each independently represents an alkyl group or a substituted or unsubstituted aryl group, R_1 and R_2 each independently represents a hydrogen atom, an alkyl group containing 1—6 carbon atoms, or a halogen atom, and —(A)— represents a member selected from the group consisting of (III)—(IX) wherein

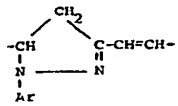
is (III)

is (IV)



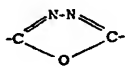
is (V)

wherein Z_1 and Z_2 each independently represents an alkyl group containing 1—6 carbon atoms, or a substituted or unsubstituted aryl group, and R_3 represents a hydrogen atom or an alkyl group containing 1—6 carbon atoms,

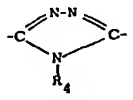


is (VI)

wherein Ar represents a substituted or unsubstituted aryl group,

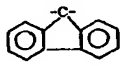


is (VII)



is (VIII)

wherein R_4 represents an alkyl group containing 1—6 carbon atoms, and



is (IX)

2. An electrophotographic photosensitive body according to Claim 1, wherein said salt having an oxidizing ability is a salt of an optional combination between an anion selected from among $[SbCl_6]^-$, $[SbCl_4]^-$, $[PF_6]^-$, $[BF_4]^-$, and $[C10_4]^-$ and a cation selected from among [tropylium]$^+$, [triphenylmethyl]$^+$, [(p-bromophenyl)ammonium]$^+$, [tetraethylammonium]$^+$, [benzyldimethylphenylammonium]$^+$, [2,4,6-trimethylpyrylium]$^+$, Ag^+, K^+, and Na^+.

3. An electrophotographic photosensitive body according to Claim 1 or Claim 2, wherein said protective layer contains 5 to 100 parts by weight of aromatic compound as defined in Claim 1 and 0.01 to 10 parts by weight of salt having an oxidizing ability per 100 parts by weight of the binder resin.

4. An electrophotographic photosensitive body according to any one of Claims 1 to 3, wherein the thickness of said protective layer is from 2 to 30 microns.

5. An electrophotographic photosensitive body substantially as described in any one of the foregoing Examples 1 to 3.

6. An electrophotographic imaging apparatus, the apparatus comprising: an electrophotographic photosensitive body in accordance with any one of Claims 1 to 5; means to uniformly electrostatically charge said body; means to expose the photoconductive layer of the thus-charged body imagewise to actinic electromagnetic radiation to form an electrostatic latent image; and means to develop the electrostatic latent image.

7. An electrophotographic imaging method, the method comprising: uniformly electrostatically charging an electrophotographic photosensitive body in accordance with any one of Claims 1 to 5; imagewise exposing the photoconductive layer of the thus-charged body to actinic electromagnetic radiation to form an electrostatic latent image; and developing the electrostatic latent image.

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